UNIVERSITY OF SWAZILAND
MAIN EXAMINATION 2017/2018

TITLE OF PAPER	:	Organic Chemistry 1
COURSE NUMBER	:	C303
TIME	:	Three Hours
INSTRUCTIONS	:	Answer any **Two Questions** from **Section A** and any **Two Questions** from **Section B**.

This Paper contains five (9) pages.

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SECTION A

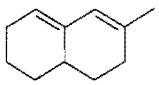
SPECTROSCOPY AND STRUCTURE ELUCIDATION

Question 1

(a) Define the following terms;
(i) Spectroscopy
(ii) Auxochrome
(iii)Bathochromic Shift
(iv)Index of hydrogen deficiency
(v) Fingerprint region [5]

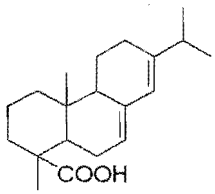
(b) Explain the differences in λ_{max} in cisoid and transoid UV absorptions. [3]

(c) A diene $C_{11}H_{16}$ was thought to have the structure below. Its UV spectrum showed a λ_{max} of 263 nm. Can the structure below be correct? If not, draw the structure with the same skeleton that satisfies the spectral data

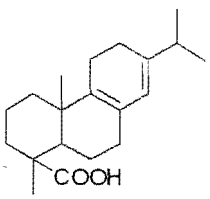


[3]

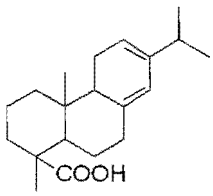
(d) Can you distinguish between the following three isomeric acids by UV spectroscopy? Use the Woodward-Fieser rules to predict each λ_{max}. [6]



A



B



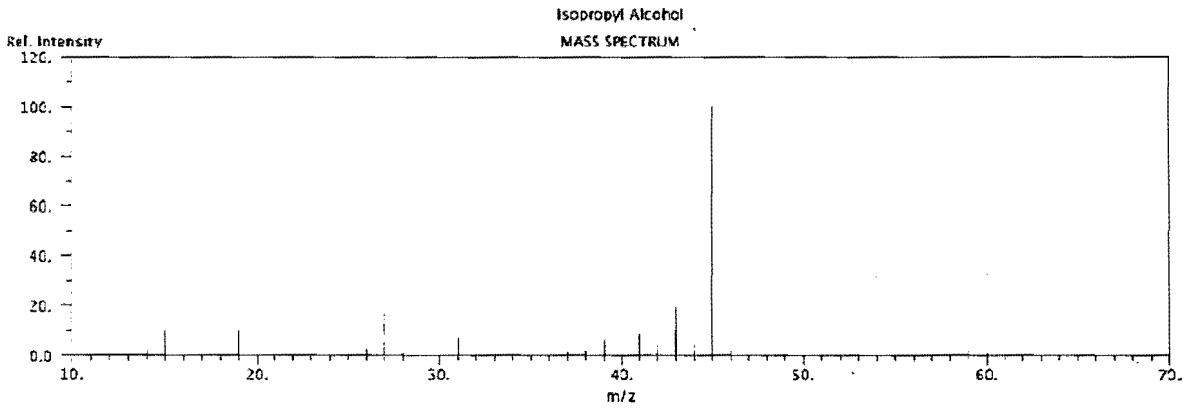
C

(e) Propose a structure for an alcohol $C_4H_{10}O$ that has the following;
^{13}C NMR Spectral data:
Broadband-decoupled ^{13}C NMR: 19.0, 31.7, 69.5 δ
DEPT-90: 31.7 δ
DEPT-135: positive peak at 19.0 δ, 31.7 δ , negative peak at 69.5 δ [8]

Question 2

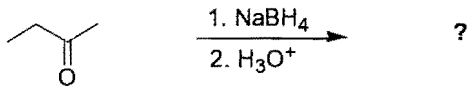
(a) The electron impact ionization (EI) mass spectrum for 2-propanol is shown below. Write Lewis structures for the species that give rise to the peaks at m/z 45 and m/z 43. Make sure to show all carbon, hydrogen, and oxygen atoms and all bonds, charges, lone pairs of electrons, and unpaired electrons.

[6]



(b) Write the products of the following reactions. Propose plausible IR absorption bands and m/z of the products.

(i)



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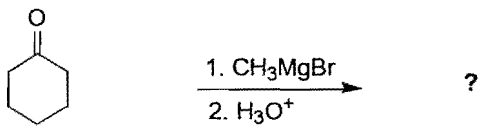

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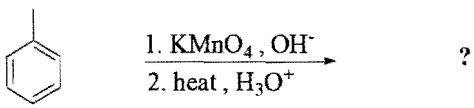
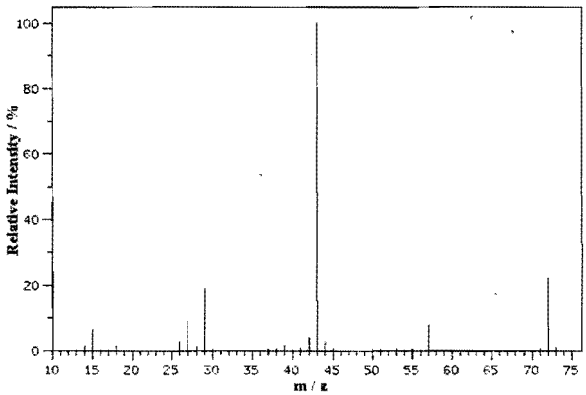


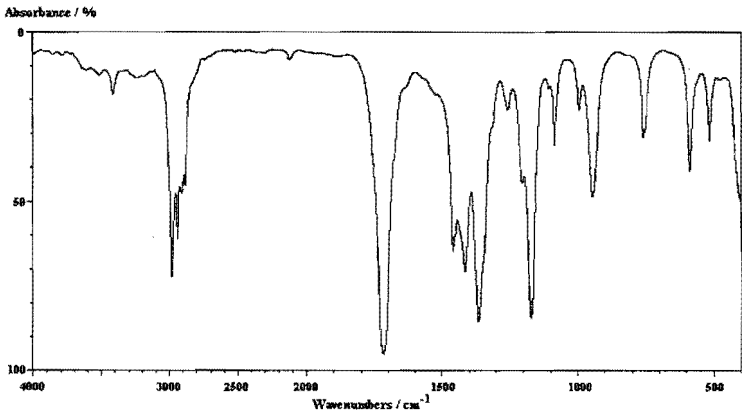
[9]

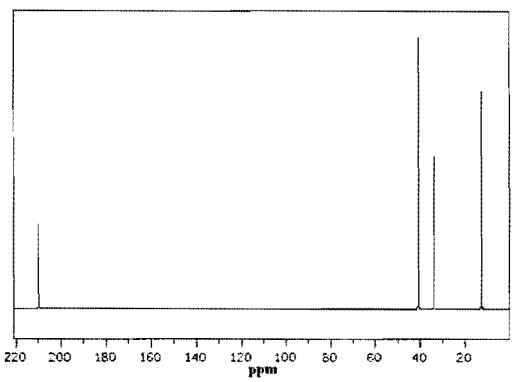
Question 3

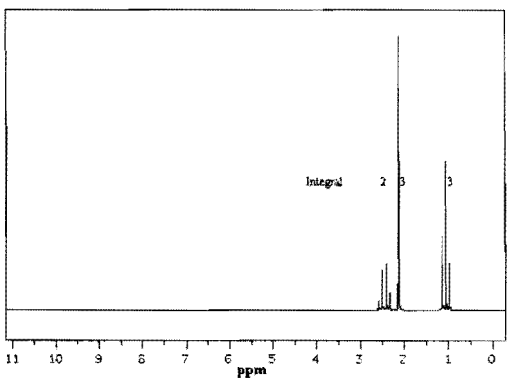
(a) The following spectral data (CI mass spectrum, infra-red, ^{13}C-nmr and H-nmr) is provided for an unknown compound. You are required to deduce the **structure** of the unknown compound that is consistent with all the data provided. **[20]**

(i)

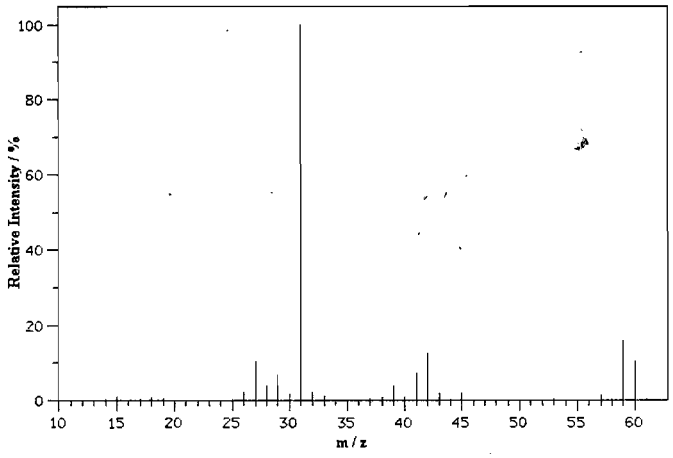


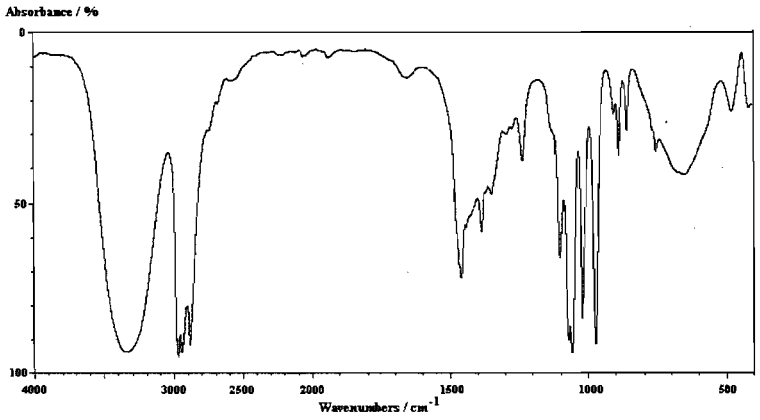


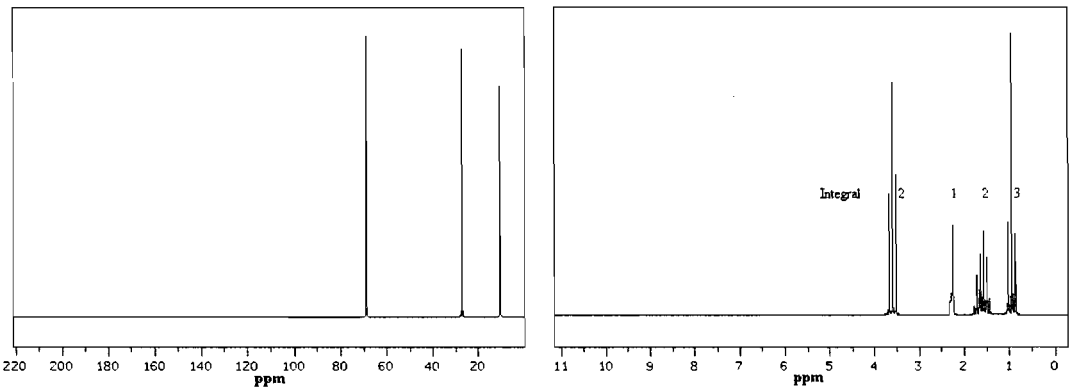




(ii)







(b) When the ^1H NMR spectrum of acetone, CH_3COCH_3, is recorded on an instrument operating at 200 MHz, a single sharp resonance at 2.1 δ is seen.

(i) How many hertz downfield from TMS does the acetone resonance correspond to?

(ii) If the ^1H NMR spectrum of acetone were recorded at 500 MHz, what would the position of the absorption be in δ units?

(iii) How many hertz from TMS does this 500 MHz resonance correspond to?

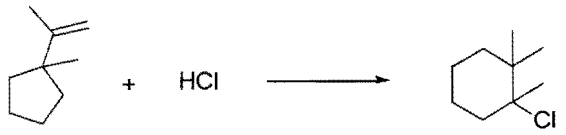
[5]

SECTION B: REACTION AND SYNTHESIS OF ORGANIC COMPOUNDS

Question 4

(a) (i) Addition of HCl to 1-isopropenyl-1-methylcyclopentane yields 1-chloro-1,2,2-trimethylcyclohexane. Suggest a mechanism, showing the structures of the intermediate and using curved arrows to indicate electron flow.

[6]



(ii) Draw an energy diagram for the reaction, labeling all points of interest and making sure that the relative energy levels on the diagram are consistent with the information given. [6]

(b) (i) The reaction of hydroxide ion with chloromethane to yield methanol and chloride ion is an example of a general reaction type called nucleophilic substitution reaction:

$$HO^- + CH_3Cl \longrightarrow CH_3OH + Cl^-$$

The value of ΔH° for the reaction is -75 kJ/mol, and the value of ΔS° is +54 J/(K.mol). What is the value of ΔG° (in kJ/mol) at 298 K? Is the reaction exothermic or endothermic? Is it exergonic or endergonic?

[6]

(ii) The addition of water to ethylene to yield ethanol has the following thermodynamic parameters:

$$H_2C=CH_2 + H_2O \longrightarrow CH_3CH_2OH$$

ΔH° = -44 kJ/mol
S° = -0.12 kJ/(K.mol)
K_{eq} = 24

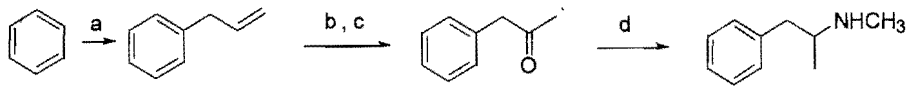
(a) Is the reaction exothermic or endothermic?
(b) Is the reaction favorable (spontaneous) or unfavorable (nonspontaneous) at room temperature (298 K)?

[7]

Question 5

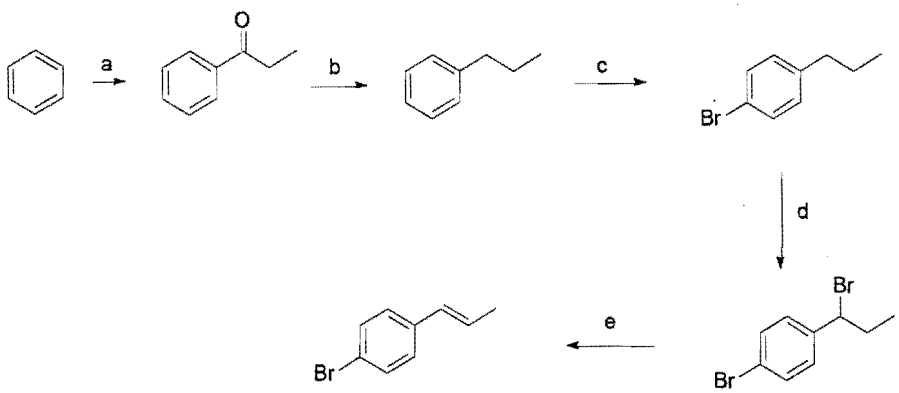
(a) Fill in the reagents a – d in the following synthesis of racemic methamphetamine from benzene.

[12]



(b) Identify the reagents represented by the letters a-e in the following scheme.

[13]



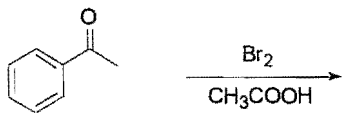
Question 6

(a) (i) Name the four kinds of organic reactions. [4]
(ii) Give an appropriate example for each named reaction. [4]
(iii)What is a reaction mechanism? [2]
(iv) Name two general types of reactions by which reactions occur, and give one real example for each type.

[5]

(b) Write the structure of the major product expected from the following reactions.

(i)



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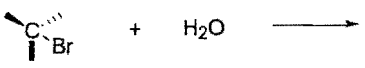

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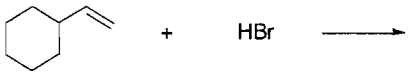
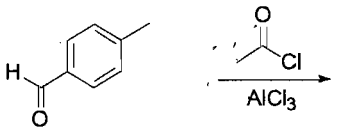


(iv)



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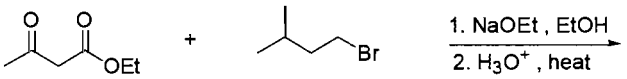

[10]

TABLE 1.3 Relative Isotope Abundances of Common Elements.

Elements	Isotope	Relative Abundance	Isotope	Relative Abundance	Isotope	Relative Abundance
Carbon	^{12}C	100	^{13}C	1.11		
Hydrogen	^{1}H	100	^{2}H	0.016		
Nitrogen	^{14}N	100	^{15}N	0.38		
Oxygen	^{16}O	100	^{17}O	0.04	^{18}O	0.2
Fluorine	^{19}F	100				
Silicon	^{28}Si	100	^{29}Si	5.1	^{30}Si	3.35
Phosphorus	^{31}P	100				
Sulfur	^{32}S	100	^{33}S	0.78	^{34}S	4.4
Chlorine	^{35}Cl	100			^{37}Cl	32.5
Bromine	^{79}Br	100			^{81}Br	98
Iodine	^{127}I	100				

1												13	14	15	16	17	18
1 H 1.008	2																2 He 4.0026
3 Li 6.94	4 Be 9.0122											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305	3	4	5	6	7	8	9	10	11	12	13 Al 26.982	14 Si 28.085	15 P 30.974	16 S 32.06	17 Cl 35.45	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.630	33 As 74.922	34 Se 78.97	35 Br 79.904	36 Kr 83.798
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.95	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57-71 *	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89-103 #	104 Rf (265)	105 Db (268)	106 Sg (271)	107 Bh (270)	108 Hs (277)	109 Mt (276)	110 Ds (281)	111 Rg (280)	112 Cn (285)	113 Nh (286)	114 Fl (289)	115 Mc (289)	116 Lv (293)	117 Ts (294)	118 Og (294)

* Lanthanide series	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
# Actinide series	89 Ac (227)	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)